In Situ Measurement of the Free Energy of Soil Moisture by Small Hygrometers (Part 1)

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Abstract

A small hygrometer with a sensing element made of magnetite colloid was tested in the laboratory and the field to decide the range of the free energy of the soil moisture within which it can be used with advantage. The results of the tests and the comparison of the different methods for the in situ measurement led to the conclusion that the hygrometer (called 'humisensor') is the best method within the range from pF 4 to pF 6.

1. Introduction

It is obvious that the in situ measurement of both the soil moisture θ and the total potential ϕ is necessary for the investigation of the physical aspect of the unsaturated flow of the soil moisture. In situ measurement of the soil moisture has been much improved by the use of neutron probes. As for the in situ measurement of the total potential, no decisive methods have been found as yet. The tensiometer is available only when the pF value is lower than 2.8. The electric resistance block, gypsum block, and dielectric block are of poor reliability because of the ambiguity in their principles of measurement[1]. At the present time the hygrometer and the psychrometer seem the most promising[1], though they are at present incomplete methods.

Recent development of hygrometers for industrial use have made it possible to use small, reliable, and durable hygrometers[2]. Some of them are applicable to the in situ measurement of the humidity of the soil air under the ground. In this paper the performance of a magnetite hygrometer as a sensor of the total potential of the soil moisture will be tested.

2. Principles of measurement

The principles of the hygrometer and psychrometer methods have been developed on the basis of the free energy concept of soil moisture[1]. In this chapter a brief review of the principles is given with some comments. Usually the system composed of the soil air and the soil water can be approximately regarded as isothermal and isobaric. The increment of Gibbs' free energy G of the system by the small increment of water is written as[1],

$$f\equiv\left(\frac{\partial G}{\partial m}\right)_{T,P}=\left(\frac{\partial U}{\partial m}\right)_{T,P}-T\left(\frac{\partial S}{\partial m}\right)_{T,P}+P\left(\frac{\partial V}{\partial m}\right)_{T,P}$$
$$\equiv u-Ts+Pv \qquad (1)$$

where m is the quantity of water in the system, T the temperature, and P

the pressure. The quantities U, S, and V are the total internal energy, the entropy, and the volume, respectively, of the system. It must be noted that P is not the pressure in the soil water but the pressure around the system (i. e. the atmospheric pressure). The quantity f is often called the 'potential'[3] or the 'free energy'[1] of soil moisture.

When the infinitesimal quantity of water δm moves from a part of the soil where $G=G_1$ to another part where $G=G_2$, the increase of G as a whole must be zero or negative according to the principle of thermodynamics.

$$\delta G=-\left(\frac{\partial G_1}{\partial m}\right)_{T,P}\delta m+\left(\frac{\partial G_2}{\partial m}\right)_{T,P}\delta m=-(f_1-f_2)\delta m\leqq 0 \tag{2}$$

Therefore the movement is possible when $f_1>f_2$. When $f_1=f_2$ the two parts of the soil are in equilibrium.

If the free pure water (situation A) at the temperature T and under the atmospheric pressure P receives the reversible change of $\varDelta f$ by the reversible changes of $\varDelta P$, $\varDelta T$, and the receipt of the mechanical work $\varDelta w_m$ (situation B), and becomes in equilibrium with the soil moisture (situation C) at the temperature T and under the atmospheric pressure P, the following relations hold[1].

$$f_B=f_C \tag{3}$$

$$\varDelta f\equiv f_B-f_A=f_C-f_A=v\varDelta P-s\varDelta T+\varDelta w_m \tag{4}$$

In this case $\varDelta P$ coincides with the change of the pressure in the water. The quantity $\varDelta f$ is equal to the free energy of the soil moisture relative to the free pure water. It will be simply called the 'free energy' of soil moisture in the following. Assuming that the flow rate of the soil moisture is proportional to the gradient of $\varDelta f$, the fundamental equation of the flow of the unsaturated soil moisture under the isothermal condition is derived in the form[3],

$$\frac{\partial\theta}{\partial t}=\nabla\cdot[K\nabla(\varDelta f)] \tag{5}$$

where θ is the concentration of soil moisture in the soil. The quantity $\varDelta f$ is equivalent to the total potential ϕ of the soil moisture[1]. It is composed of the three components (matrix potential, osmotic potential, and gravitational potential) as,

$$\varDelta f=\varDelta f_{mat}+\varDelta f_{osm}+\varDelta f_{grav} \tag{6}$$

All the principles of measurement of the free energy or the total potential can be derived from eq. (4).[1]

When the water vapor in the soil air is in equilibrium with the soil water, the free energy of soil moisture can be gotten by putting $\varDelta T=\varDelta w_m=0$ in eq. (4) and integrating with respect to P.

$$\varDelta f=\int_{p_0}^{p}vdP=\int_{p_0}^{p}\frac{RT}{P}dP=RT\log_e\left(\frac{p}{p_0}\right)=RT\log_e H \tag{7}$$

where p is the water vapor pressure of the soil air in equilibrium with the soil water, p_0 the saturation vapor pressure of free pure water at temperature T,

R the gas constant, and H the relative humidity. If the relative humidity and the temperature of the soil air are measured, one can get the value of Δf from eq. (7). In deriving eq. (7) the mechanical work done by the gravitational force is ignored, so it must be said that the free erergy given in eq. (7) is the sum of Δf_{mat} and Δf_{osm}. The quantity Δf_{grav} can easily be calculated with the relation,

$$\Delta f_{grav} = \rho g z \tag{8}$$

where ρ is the density of water, g the acceleration of gravity, and z the height of the point of interest relative to the datum level. Differentiating eq. (7) we get,

$$\delta(\Delta f) = RT\frac{\delta H}{H} \tag{9}$$

3. The humisensor

The measurement of the humidity of the soil air can be carried out by the psychrometer or hygrometer method. Since it is a property of the psychrometer that the deficit of vapor pressure from saturation is measured, it seems very suitable to our purpose (see eq. (7) and (9)). The psychrometers for field measurement are the thermocouple psychrometer[4)] or the thermister psychrometer[5)] at the present time. It has been shown that the thermister psychrometer can measure the free energy of the soil moisture within an accuracy of 3 % in the range from pF 2 to pF 5, if the difference in the soil temperature between the positions of the dry bulb and the wet bulb is less than 0.001°C[5)]. At the present time the psychrometric methods can not be used for in situ measure ment because of the difficulty in the maintenance of the wet bulb and in the temperature regulation.

The hygrometers have, in general, shown good performance at the lower humidity ranges, but can not measure the free energy at low suction ranges precisely. The gypsum block may be regarded as the only kind of hygrometer that has been used for the measurement of the free energy of the soil moisture since some time ago. Though it has been widely used, it is of poor reliability because of the ambiguity in its principles of measurement. The gray hydrocal hygrometer[6)] recently developed is excellent with regard to accuracy and durability, but it must be dried before measurement to avoid the hysteresis error. Its large size also make it unsuitable for use in making in situ measurements.

Recent developments in industrial instrumentation have produced small, precise, and durable hygrometer sensors, among which the magnetite hygrometer called the 'humisensor'* seems the most fitted to our purpose. The humisensor consists of the magnetite colloid attached to a steatite disc. The magnetite colloid changes its electric resistance according to the relative humidity of the surrounding air, and the electric resistance is detected through the comb-shaped electrodes buried in the magnetite colloid. The usual cover of the humisensor is

* A product of Tamura Chemical Laboratories produced under patent No. 500464 held by the Japanese Government.

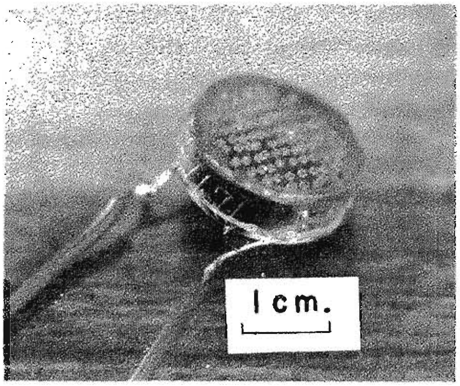

Fig. 1. A humisensor with plastic cover.

not suited for underground use, so it must be replaced by a suitable one in order to protect the magnetite colloid from soil particles sticking to it and to minimize the space between the surface of the magnetite and the cover (see Fig. 1). The results of the fundamental test of the humisensor carried out by Kanou and Kawasaki[7] suggests that the humisensor has many merits for underground use. Its resistance has a high sensibility to change in the relative humidity (5 %/1 % R. H.) and a low sensibility to temperature change (0.2 %/1°C). It has a small size; 20 mm diameter and 1 mm thickness. It absorbs little moisture and so gives practically no disturbances to the surrounding soil moisture. It shows a rapid response to humidity change. Its chemical stability make long term use possible. On the other hand, one of the defects of the humisensor is that it reduces its performance at high humidity ranges. Though the characteristics of the humisensor at high humidity ranges are not well established as yet, it may be a fatal defect for the measurement of the free energy of the soil moisture. Therefore some further tests are needed to see whether the humisensor is useful for the in situ measurement of the free energy of the soil moisture.

4. The laboratory tests

In order to see the limit of the range of humidity in which the humisensor can be used with advantage, the time response and the hysteresis characteristics were examined at higher humidity ranges. Standard NaCl solution was put into the lower part of a separable flask, and a humisensor was set in the upper part of it with a thermometer and a stirrer (see Fig. 2). The flask was set in a constant temperature bath which can control the temperature variation to within ± 0.1°C, so that the temperature variation in the flask might be regulated to within ± 0.5°C. The humidity of the air in the flask was changed by exchanging the standard NaCl solution.

The electric circuit for the measurement of the resistance of the humisensor is shown in Fig. 3. The output voltage from the oscillator is divided by the humisensor and the base resistance (selected from $3\,K\Omega$ and $5\,M\Omega$), rectified by the bridge of the diodes, and recorded with a strip chart recorder. The circuit is available not only for laboratory tests but also for general use. An example of the time response of the humisensor is shown in Fig. 4. The depressions in the reading of the humisensor at the moistening stage were due to the exposure of the humisensor to the open air while the NaCl solution was being exchanged. It is seen from the figure that the time response of the humisensor is slower at the higher humidity ranges than at the lower humidity ranges, and slower at the desiccating stage than at the moistening stage. The calibration curves of the resistance of the humisensor versus the relative

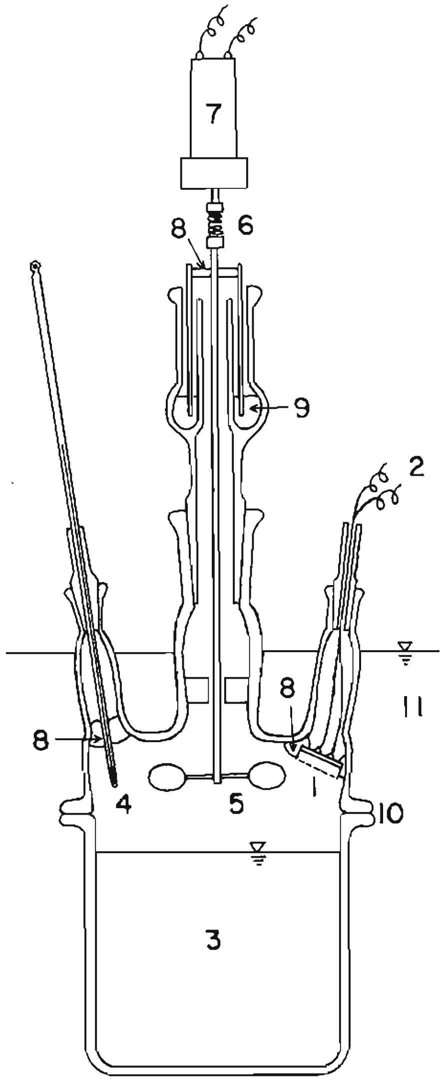

Fig. 2. The equipment for the laboratory test.
1-humisensor,
2-lead of the humisensor,
3-NaCl solution,
4-thermometer,
5-air stirrer,
6-flexible joint,
7-geared motor,
8-seals,
9-sealing water,
10-ground glass sealing,
11-the water of constant temperature bath.

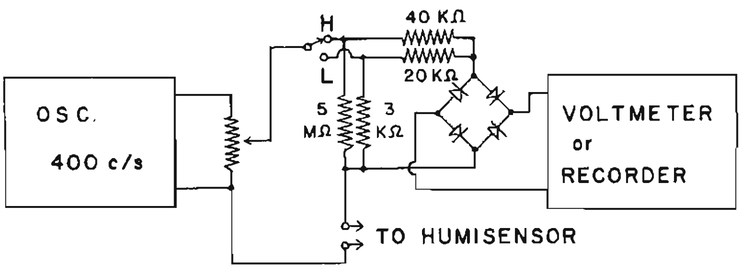

Fig. 3. The electric circuit for the measurement or recording of the electric resistance of the humisensor.

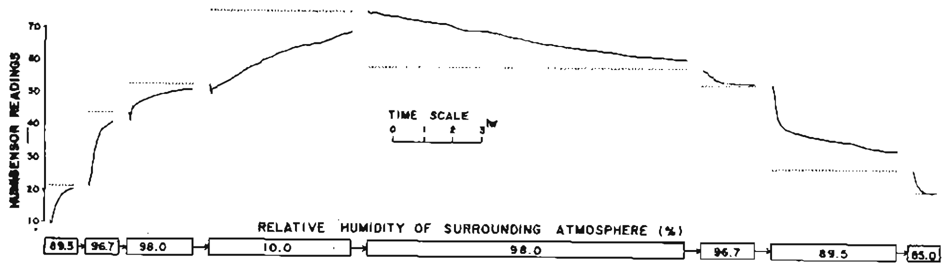

Fig. 4. An example of the time response of humisensor (at 15°C). The dotted lines show the ultimate readings.

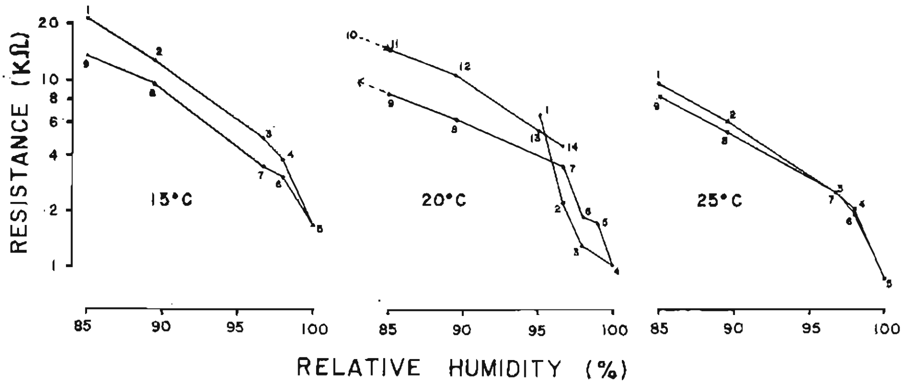

Fig. 5. The calibration curves of the humisensor at different temperature. The numbers given to each points show the sequence of the operation.

humidity at different temperatures are shown in Fig. 5. From the figure it seems as if the hysteresis error is larger at the lower humidity ranges. It is contradictory to the results of the tests carried out by Kanou and Kawasaki[7] that the hysteresis error of the humisensor may be less than 1 % at humidity lower than 95 % R. H. though a much greater hysteresis error may take place at humidity over 95 % R. H. The major cause of the contradiction can be ascribed to the difference in the time taken for the resistance of the humisensor to attain an ultimate value, because Table 1 shows that a shorter time was taken for the measurement at the lower humidity range. Therefore it may be concluded that the difference in the resistance of the humisensor between the

TABLE 1.
An example of the time taken for the measurement of the elecric resistance of the humisensor at different stages (at 25°C).

Relative humidity		85.0	89.5	96.7	98.0	100.0
The time taken for the measuremen	moistening stage	3	2	2.5	17	21
	Desiccating stage	2	20	7	200	—

desiccating and moistening stages is mainly caused by the insufficient time taken for the measurement, and that an accuracy as good as 1 % R. H. is possible at all ranges of humidity when sufficient time is taken for the measurement. If the time taken for the measurement is five hours, the accuracy may be about 2 % R. H. at humidity below 95 % R. H. and about 5 % R. H. at humidity near saturation. Fig. 5 also shows that the reading of the humisensor has a positive temperature coefficient. A calibration curve of the humisensor as a sensor of the free energy of the soil moisture at 25°C is given in Fig. 6. The calibration curve at the humidity range 30-80 % R. H. made by the maker was also used for the synthesis of the calibration curves.

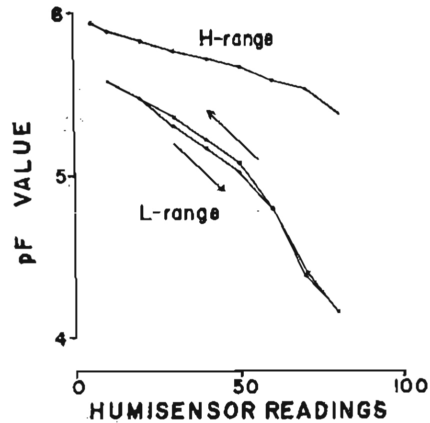

Fig. 6. The relationship between the free energy and the reading of the humisensor at 25°C.

5. The field test

In order to ascertain the applicability of the humisensor to in situ measurement in the field, it was buried in sandy soil in the field at a depth of 8 cm. Continuous measurement was carried out with the electric circuit described above from April 4 th to May 13 th 1968. The result of the measurement was characterized by a large daily variation in the free energy of the soil moisture. In the daytime the free energy dropped by about 4×10^5 cm. water if it was fine weather. A typical example of the daily variation is shown in Fig. 7. It

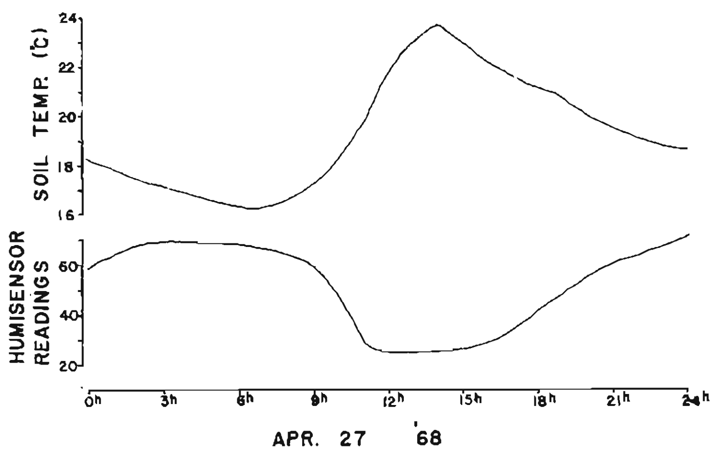

Fig. 7. An example of the daily variation in the reading of humisensor and the soil temperature both at the depth of 8 cm.

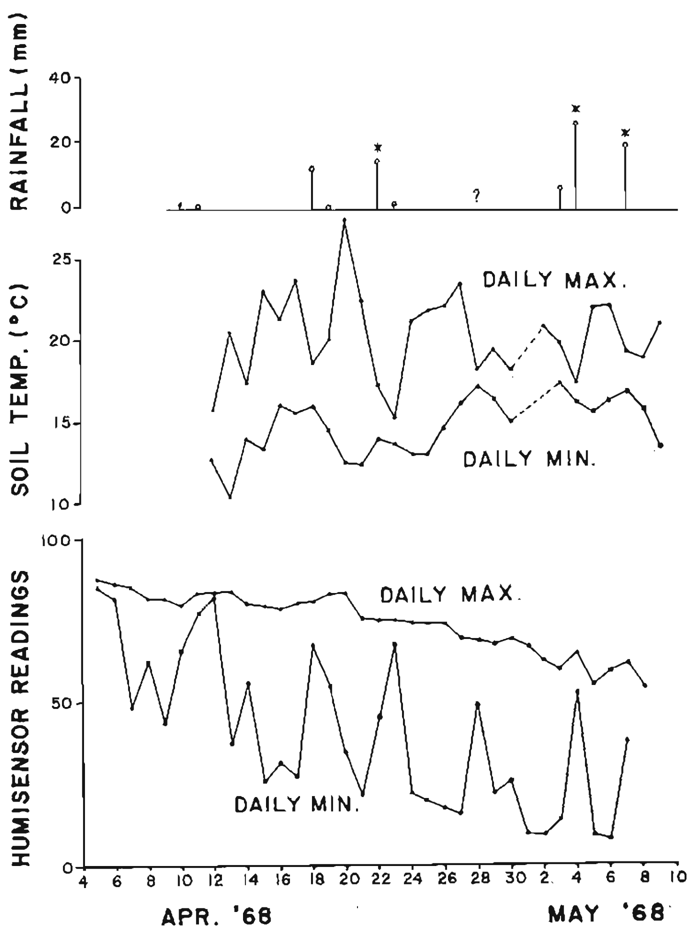

Fig. 8. The daily maximums and minimums in the reading of the humisensor and of the soil temperature both at the depth of 8 cm. * uncertain measurement of rainfall.

is seen that the variation in the reading of the humisensor is well correlated with the soil temperature at the same depth (8 cm). Fig. 8 shows the daily maximums and minimums in the reading of the humisensor and the soil temperature at the depth of 8 cm. with the daily rainfall. It is seen that the daily minimum of the reading of the humisensor and the daily maximum of the soil temperature which occurred almost at the same time are closely correlated. These phenomena can not be explained by the temperature dependence of the humisensor, because the direction of the daily variation in the reading of the humisensor is the opposite of the temperature dependence shown in Fig. 5. Fig. 7 shows that the phases of the variations in the reading of the humisensor and in the soil temperature differ a little. Kikkawa and Kawanishi[8] found that the moisture can be extracted from the water table at the depth of 50cm. through evapotranspiration by weeds. Therefore it is reasonable to suppose that the daily variation in the reading of the humisensor was caused by evapotrans-

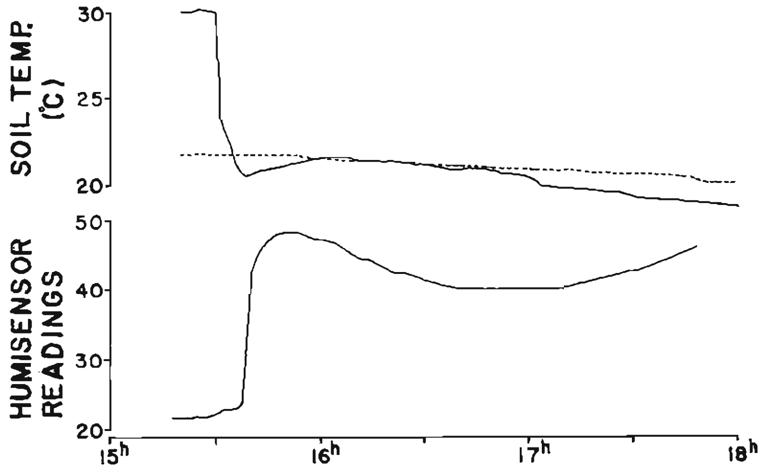

Fig. 9. The effect of the sprikling of water on the soil temperature at the depth of 1 cm. (the solid line) and 8 cm. (the dotted line), and on the reading of the humisensor at the depth of 8 cm.

piration. It has been shown that transpiration by plants has a fast response to variation in the solar radiation[9], and it is certain that the daily variation in the soil temperature was also caused by the solar radiation. The fact of the extraction of the soil moisture could not be ascertained by the measurement of the soil moisture by the weighing method because of a large sampling error.

The effect of rainfall on the daily maximum of the reading of the humisensor is obvious in Fig. 8, though the effect of it on the daily minimum is not obvious. The effect of the sprinkling of water on the reading of the humisensor is shown in Fig. 9. The effect of the sprinkling appeared in the soil temperature at a depth of 1 cm. as soon as the water was sprinkled, and in the reading of the humisensor about six minutes later. The soil temperature at the same depth (8 cm.) with the humisensor received almost no influence.

A steady trend of decrease in the reading of the humisensor is recognized in Fig. 8. The period of the field test was in the growing season, and weeds were growing over the ground under which the humisensor and the thermisters were buried. After the field test, the humisensor was tested again in the laboratory, and no change in the calibration curve was found. Therefore the increasing rate of transpiration of the weeds is thought to have been the cause of the decreasing trend.

The minimum value of the free energy of the soil moisture measured in this experiment was as low as -10^6 cm. water, which far exceeded the permanent wilting point of sunflowers[10]. It is difficult to explain why the weeds did not wilt, though the weeds might be able to endure the dry conditions somewhat more than sunflowers. On the other hand, the maximum reading of the humisensor during this experiment exceeded the value which is equivalent to 100% R. H., possibly owing to dewing.

6. Discussion and conclusions

The results of the tests described above make it possible to decide the range of the free energy in which the humisensor can be used with advantage. The practical accuracy of the humisensor was about 1 % R. H. in the static state. From eq. (9) we see that an error of 1 % R. H. in the relative humidity causes an error of 1.4×10^4 cm. water in the free energy near 100 % R. H. ($\Delta f \doteqdot 0$), and that of 2.8×10^4 cm. water at 50 % R. H. ($\Delta f = -10^6$ cm. water) at 25°C. It is seen that the higher the humidity, the lower is the accuracy of the measurement of the free energy, and that the humisensor can not be used when the free energy is higher than -1.4×10^4 cm. water (pF 4.15). The difficulty in maintaining good electrical insulation in field conditions may limit the measurable humidity to above 50 % R. H. (pF = 6).

Table 2 compares the different field methods of measuring the free energy of the soil moisture. Though we can not measure all the components of the free energy by any single method, the measurement of the components Δf_{mat} and Δf_{osm} is sufficient because Δf_{grav} can be easily calculated by eq. (8). Since no methods can cover the whole range of free energy encountered under natural conditions, it is necessary to combine the different methods, such as tensiometer, gypsum block, and humisensor. It is concluded from Table 2 that the humisensor can be used with advantage in the range of the free energy from about pF 4 to pF 6. If the improvement of the humisensor or the development of new typers of hygrometer are realized to measure the relative humidity to an accuracy of 0.05 % R. H. or less, it will become possible to extend the upper limit of the range of measurement of the free energy to -7×10^2 cm. water and to do without the use of the gypsum block.

Concerning the durability of the humisensor during continuous measurements in field conditions, it was ascertained that continuous use under the ground at

TABLE 2.

A comparison of the different methods of measuring the components of the free energy of the unsaturated soil moisture in the field (composed with reference to the literatures[1,5,6])

Methods	Range (absolute value in cm. water)	Measurable components	Fitness for in situ measurement	Accuracy	Response
Tensiometer	$0-7\times10^2$	$\Delta f_{mat}+\Delta f_{grav}$	yes	good	fast
Gypsum block	$4\times10^2-4\times10^4$	Δf_{mat}	yes	not good	slow
Electric resistance block*	10^2-10^5	(indirectly) Δf_{mat}	yes	not good	fast
Dielectric block*	10^2-10^5	(indirectly) Δf_{mat}	yes	not good	fast
Thermister psychrometer	10^2-10^5	$\Delta f_{mat}+\Delta f_{osm}$	no	good	fast
Gray cal hygrometer	$0-3\times10^6$	$\Delta f_{mat}+\Delta f_{osm}$	no	good	average
Humisensor	10^4-10^6	$\Delta f_{mat}+\Delta f_{osm}$	yes	average	fast

* Properly the methods for the measurement of the soil moisture

least during fourty days brings no change on the calibration curve of the humisensor when the field condition is not very severe. The stability of the calibration curve during a period of a year has been ascertained in a laboratory test.[7] Though the humisensor is stable both physically and chemically, the filling of the space between the element and the cover of the humisensor with saline ground water or corrosive gas may ruin it.

The question remaining unsolved in chapter 5 may be solved when the transient response of the humisensor under fast change in the soil temperature is clarified. The validity of the assumption that the vapor in the soil air is in equilibrium with the soil water may be the key to the problem. This problem will be fully discussed in the next part of this paper.

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